# Routes to Regioselective Deuteriation of Heteroaromatic Compounds

Browne, Wesley R.; O'Connor, Christine M.; Killeen, J. Scott; Guckian, Adrian L.; Burke, Micheal; James, Paraic; Burke, Maurice; Vos, Johannes G.

*Published in:*
Inorganic Chemistry

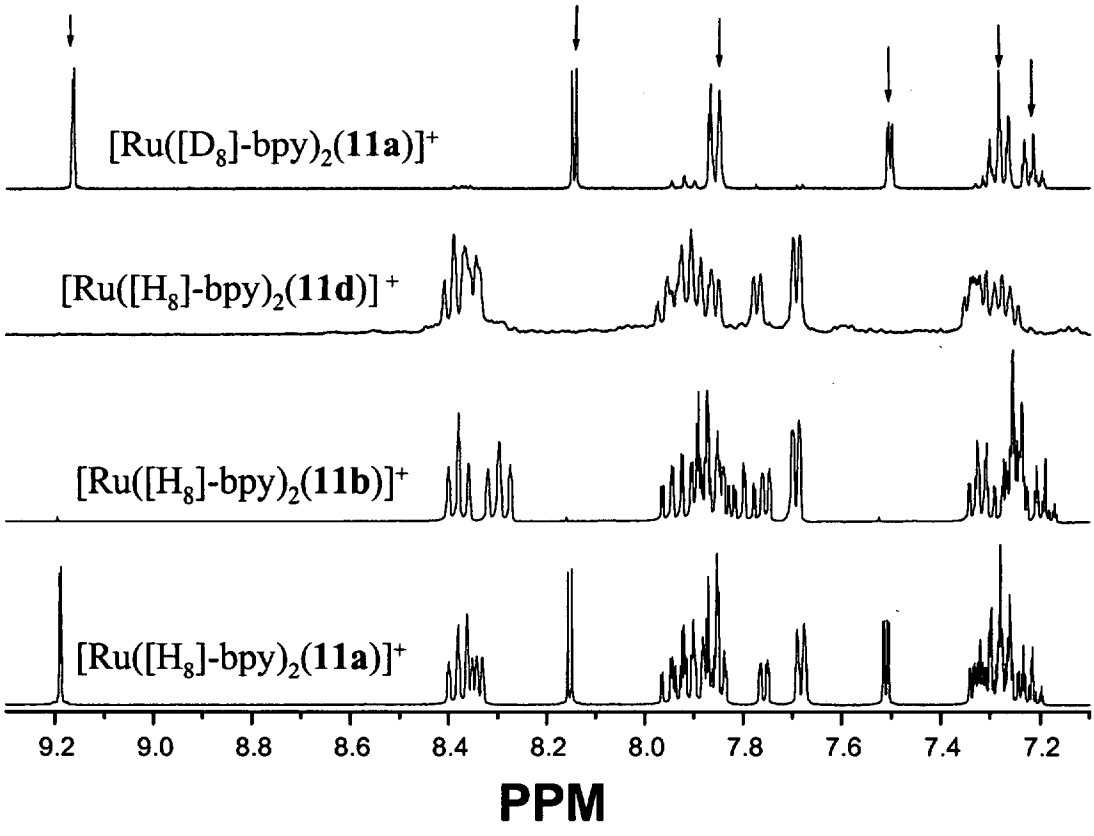
*DOI:*
10.1021/ic020226y



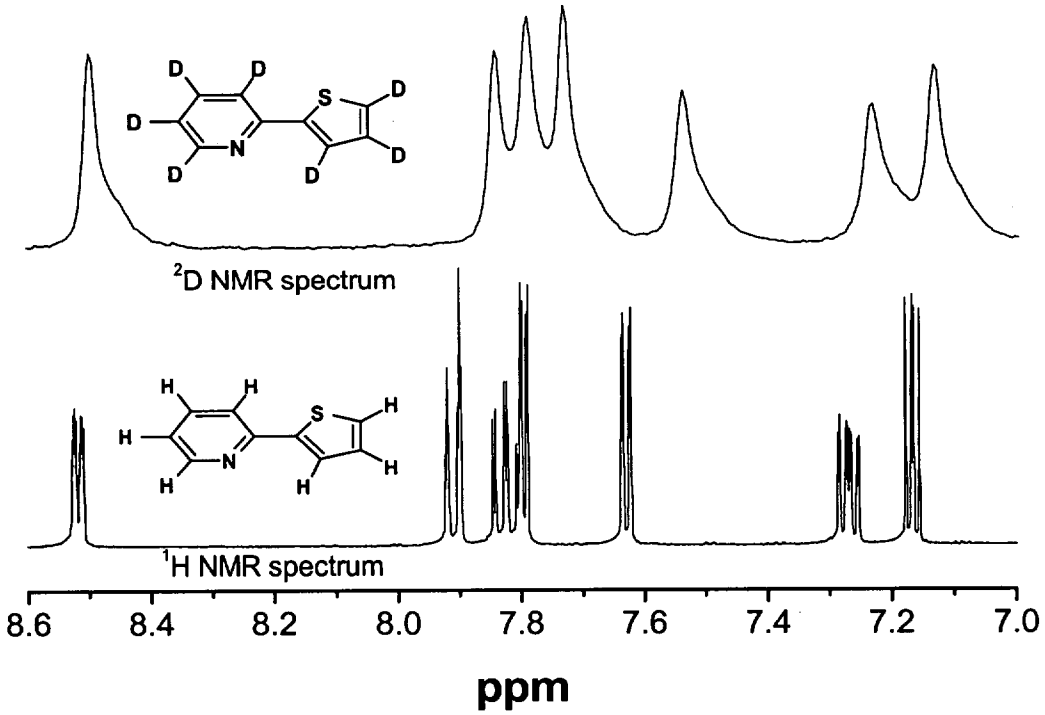
*Publication date:*
2002

**Supplementary information**

(S1) $^1$H NMR spectra (400 MHz) of [Ru([$D_x$]-bpy)([$D_y$]-phpztr)]($PF_6$) in $d_3$-acetonitrile (x= 0 or 8, y = 0, 3, 8). phpztr$^-$ (**11**) resonances are indicated by arrows.



(S2) $^{1}H$ NMR spectra of $[H_7]$-2-(thein-2'-yl)-pyridine (**8a**) (lower spectrum) in $[D_6]$-acetone and $^{2}D$ NMR spectra of $[D_7]$-2-(thein-2'-yl)-pyridine (**8c**) (upper spectrum) in $[D_6]$-acetone



(S3) $^{1}H$, $^{2}D$ $^{13}C$ NMR Spectroscopic data and Mass spectral data for all partially and fully deuteriated compounds described in Tables 1 and 2.

*Symmetric Diimine compounds*

[$D_8$]-2,2'-bipyridine **1b**: Mass spectroscopy $HM^{+\cdot}$ ion at 165 m/z. $^{1}H$ NMR in [$D_6$]-DMSO δ ppm; 8.69 (H3, *resid.* s), 8.39 (H6, *resid.* s), 7.95 (H4, *resid.* s), 7.45 (H5, *resid.* s). $^{13}C$ NMR in [$D_6$]-DMSO δ ppm; 149.62 (C3, t), 120.79 (C6, t), 137.68 (C4, t), 124.56 (C5, t), 155.54 (C2, s). $^{2}D$ NMR in [$H_6$]-acetone δ ppm; 8.68 (D3), 8.5 (D6), 7.89 (D4), 7.39 (D5)

[$D_4$]-4,4'-bipyridine **2b**: Mass spectroscopy $HM^{+\cdot}$ ion at 161 m/z. $^{1}H$ NMR in [$D_6$]-DMSO δ ppm; 8.72 (H2, *resid.* s), 7.82 (H3, s). $^{13}C$ NMR in [$D_6$]-DMSO δ ppm; 150.89 (C2/6, t)), 121.64 (C3/5, s), 144.67 (C4, s). $^{2}D$ NMR in [$H_6$]-acetone δ ppm; 8.71 (H2/H6, s), 7.76 (H3/H5, *resid.* s).

[$D_8$]-4,4'-bipyridine **2c**: Mass spectroscopy $HM^{+}$ ion at 165 m/z. $^{1}H$ NMR in [$D_6$]-DMSO δ ppm; 8.72 (H2/6, *resid.* s), 7.82 (H3/5, *resid.* s). $^{13}C$ NMR in [$D_6$]-DMSO δ ppm; 150.89 (C2/6, t)), 121.64 (C3/5, t), 144.67 (C4, s). $^{2}D$ NMR in [$H_6$]-acetone δ ppm; 8.71 (H2/H6, s), 7.76 (H3/H5, s)

[$D_{12}$]-4,4'-dimethyl-2,2'-bipyridine **3b**: Mass spectroscopy $HM^{+\cdot}$ ion at 197 m/z. $^{1}H$ NMR in [$D_6$]-DMSO δ ppm ; 2.36 (Me, m), 8.51(H6, *resid.* s), 8.20 (H3, *resid.* s), 7.27 (H5, *resid.* s). $^{13}C$ NMR in [$D_6$]-DMSO δ ppm; 149.32 (C6, t), 121.58 (C3, t), 148.28 (C4, s), 125.25 (C5, t), 155.45(C2, s) 21.23 (Methyl-, not observed). $^{2}D$ NMR in [$H_6$]-acetone δ ppm; 2.35($CD_3$-), 8.49 (D6), 8.29 (D3), 7.21 (D5).

[$D_8$]-1,10-phenanthroline **4b**: Mass spectroscopy $HM^{+\cdot}$ ion at 189 m/z. $^1H$ NMR in [$D_6$]-DMSO δ ppm ; 9.10(H2/9, *resid.* s), 7.77(H3/8, *resid.* s), 8.49 (H4/7, *resid.* s), 7.99 (H5/6, *resid.* s). $^{13}C$ NMR in [$D_6$]-DMSO δ ppm; 150.31 (C2/9, t), 123.70 (C3/8, t), 136.58 (C4/7, t), 127.04 (C5/6, t), 128.75 (C11/13, s), 145.83 (C12/14, s). $^2D$ NMR in [$H_6$]-acetone δ ppm; 8.66 (D2/9), 8.46 (D4/7), 7.64 (D5/6 and D3/8))

[$D_6$]-4,7-diphenyl-1,10-phenanthroline **5b**: Mass spectroscopy $HM^{+\cdot}$ ion at 339 m/z. $^1H$ NMR in [$D_6$]-chloroform δ ppm ; 9.36 (H2/9, *resid.* s), 7.70 (H3/8, *resid.* s), 7.64 (phenyl-4,7, *resid.* s), 7.96 (H5/6, s).

[$D_{10}$]-4,7-diphenyl-1,10-phenanthroline **5c**: Mass spectroscopy $HM^{+\cdot}$ ion at 343 m/z. $^1H$ NMR in [$D_6$]-chloroform δ ppm ; 9.36 (H2/9, d), 7.70 (H3/8, d), 7.64 (phenyl-4,7, *resid.* s), 7.96 (H5/6, s).

[$D_{14}$]-4,7-diphenyl-1,10-phenanthroline **5d**: Mass spectroscopy $HM^{+\cdot}$ ion at 347 m/z. $^1H$ NMR in [$D_6$]-chloroform δ ppm ; 9.36 (H2/9, *resid.* s), 7.70 (H3/8, *resid.* s), 7.64 (phenyl-4,7, *resid.* s), 7.96 (H5/6, s). $^2D$ NMR in [$H_6$]-acetone δ ppm; 9.2 (D2/9), 7.91 (D3/8), 7.63 (phenyl-4/7, *resid.* D5/6)

[$D_{16}$]-4,7-diphenyl-1,10-phenanthroline **5e**: Mass spectroscopy $HM^{+\cdot}$ ion at 349 m/z. $^1H$ NMR in [$D_3$]-chloroform δ ppm; 9.36 (H2/9, *resid.* s), 7.70 (H3/8, *resid.* s), 7.64 (phenyl-4,7, *resid.* s), 7.96 (H5/6, *resid.* s). $^2D$ NMR in [$H_6$]-acetone δ ppm; 9.2 (D2/9), 7.91 (D3/8), 7.63 (phenyl-4/7, D5/6)

[$D_{12}$]-2,2'-biquinoline **6b**: Mass spectroscopy $HM^{+\cdot}$ ion at 269 m/z. $^1$H NMR in [$D_6$]-DMSO δ ppm; 7.69 (*resid.* s), 7.86 (*resid.* s), 8.08 (*resid.* s), 8.19 (*resid.* s), 8.58 (*resid.* s), 8.71 (*resid.* s).

[$D_4$]-2,2'-biquinoline **6c**: Mass spectroscopy $HM^{+\cdot}$ ion at 261 m/z. $^1$H NMR in [$D_6$]-DMSO δ ppm; 7.69 (dd), 7.86 (dd), 8.08 (d), 8.19 (d), 8.58 (*resid.* s), 8.71 (*resid.* s).

*Pyrazinyl- and thienyl- pyridine compounds*

*[$D_{10}$]-2,3-Di-(pyrid-2yl)-pyrazine* **7b**: Mass spectroscopy $HM^{+\cdot}$ ion at 245 m/z. $^1$H NMR in [$D_6$]-acetone δ ppm ; 8.79 (pz, *resid.* s), 8.25 (pyH6, *resid.* s), 7.86 (pyH3, *resid.* s), 7.91 (pyH4, *resid.* s), 7.32 (pyH5, *resid.* s). $^{13}$C NMR in [$D_6$]-acetone δ ppm; 143.14 (pzC5/6, t), 152.1(pzC2/3, s), 148.49 (pyC6, t), 124.16 (pyC3, t), 137.13 (pyC4, t), 123.56 (pyC5, t), 157.2 (C2, s). $^2$D NMR in [$H_6$]-acetone δ ppm; 8.71 (pz), 8.21 (pyD6), 7.88 (pyD3/D4), 7.27 (pyD5)

*[$D_2$]-2-(thien-2'-yl)-pyridine* **8b**: Mass spectroscopy $M^{+\cdot}$ ion at 164 m/z. (thH3,d), (thH4,d), (thH5, *resid.* s), (pyH6, *resid.* s), (pyH3,d), (pyH4,dd), (pyH5,d). $^{13}$C NMR in [$D_6$]-acetone δ ppm; 144.87 (thC2,s), 125.56 (thC3, s), 128.70(thC4,s), 128.77(thC5,t), 152.15 (pyC2,s), 118.99 (pyC3,s), 137.53(pyC4,s), 122.69 (pyC5,s), 149.70 (pyC6,t). $^2$D NMR in [$H_6$]-acetone δ ppm; 7.72 (*resid.* thD3 ~ 15% ), 7.54 (thD5), 8.50 (pyD6).

*[$D_7$]-2-(thien-2'-yl)-pyridine* **8c**: Mass spectroscopy $M^{+\cdot}$ ion at 169 m/z. $^1$H NMR in [$D_6$]-acetone δ ppm ; 7.7 (thH3, *resid.* s), 7.1 (thH4, *resid.* s), 7.6 (thH5, *resid.* s), 8.5 (pyH6, *resid.* s), 7.9 (pyH3, *resid.* s), 7.8 (pyH4, *resid.* s), 7.2 (pyH5, *resid.* s). $^{13}$C NMR in [$D_6$]-acetone δ ppm; 144.87 (thC2,s),

125.56 (thC3,t), 128.70(thC4,t), 128.77(thC5,t), 152.15 (pyC2,s), 118.99 (pyC3,s), 137.53(pyC4,s), 122.69 (pyC5,s), 149.70 (pyC6,s). $^{2}$D NMR in [$H_6$]-acetone δ ppm; 7.73 (thD3), 7.13 (thD4), 7.54 (thD5), 8.50 (pyD6), 7.84 (pyD3), 7.79 (pyD4), 7.23 (pyD5).

*Pyrazine-1,2,4-triazole based compounds*

[$D_4$]-Hpztr **9b**: Mass spectroscopy $HM^+$ ion at 152 m/z. $^{1}$H NMR ([$D_6$]-DMSO) δ in ppm: 9.46 (*resid.* s, pz-H3), 8.70 (*resid.* s, pz-H5), 8.66 (*resid.* s, pz-H6), 8.25 (*resid.* s, tr-H5), $^{2}$D NMR in ([$H_6$]-DMSO) δ ppm; 9.24 (pz-D3), 8.72 (pz-D5/D6), 8.49 (tr-D5)

[$D_6$]-Hmepztr **10b**: Mass spectroscopy $HM^+$ ion at 169 m/z. $^{1}$H NMR ([$D_6$]-DMSO) δ in ppm: (*resid.* s, pz-H3), (*resid.* s, pz-H5), (*resid.* s, pz-H6), (*resid.* m, Methyl). $^{2}$D NMR in ([$H_6$]-DMSO) δ ppm; 9.07 (pz-D3), 8.63 (pz-D5/D6), 2.32 (Methyl)

[$D_3$]-Hphpztr **11b**: Mass spectroscopy $HM^+$ ion at 227 m/z. $^{1}$H NMR ([$D_6$]-DMSO) δ in ppm: 9.35 (*resid.* s, pz-H3), 8.795 (*resid.* s, pz-H5), 8.765 (*resid.* S, pz-H6), 8.11 (d, 2H, ph-H2/H6), 7.54 (dd, 2H, ph-H3/H5) 7.49 (t, 1H, ph-H4). $^{2}$D NMR in ([$H_6$]-DMSO) δ ppm; 9.33 (pz-D3), 8.75 (pz-D5/D6)

[$D_5$]-Hphpztr **11c**: Mass spectroscopy $HM^+$ ion at 229 m/z. $^{1}$H NMR ([$D_6$]-DMSO) δ in ppm: 9.35 (d, 1H, pz-H3), 8.795 (dd, 1H, pz-H5), 8.765 (d, 1H, pz-H6), 8.11 (*resid.* s, ph-H2/H6), 7.54 (*resid.* s, ph-H3/H5) 7.49 (*resid.* s, ph-H4), $^{2}$D NMR in ($H_6$-DMSO) δ ppm; 8.07 (ph-D2/D6), 7.48 (ph-D3/D4/D5)

[$D_8$]-Hphpztr **11d**: Mass spectroscopy $HM^+$ ion at 332 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: 9.35 (*resid.* s, pz-H3), 8.795 (*resid.* s, pz-H5), 8.765 (*resid.* s, pz-H6), 8.11 (*resid.* s, ph-H2/H6), 7.54 (*resid.* s, ph-H3/H5) 7.49 (*resid.* s, ph-H4). $^2D$ NMR in ([$H_6$]-DMSO) δ ppm; 9.33 (pz-D3), 8.75 (pz-D5/D6), 8.07 (ph-D2/D6), 7.48 (ph-D3/D4/D5).

[$D_3$]-Htolpztr **12b**: Mass spectroscopy $HM^+$ ion at 241 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: 9.33 (*resid.* s, pz-H3), 8.77 (*resid.* s, pz-H5/H6), 7.34 (d, 2H, ph-H2/H6), 8.00 (dd, 2H, ph-H3/H5), 2.36 (s, 3H, $-CH_3$). $^2D$ NMR in ([$H_6$]-DMSO) δ ppm; 9.34 (pz-D3), 8.74 (pz-D5/D6)

[$D_3$]-Htolpztr **12c**: Mass spectroscopy $HM^+$ ion at 241 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: 9.33 (d, 1H, pz-H3), 8.77 (m, 2H, pz-H5/H6), 7.34 (d, 2H, ph-H2/H6), 8.00 (dd, 2H, ph-H3/H5), 2.36 (*resid.* m, methyl). $^2D$ NMR in ([$H_6$]-DMSO) δ ppm; 2.28 (Methyl-)

[$D_4$]-Htolpztr **12d**: Mass spectroscopy $HM^+$ ion at 242 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: (d, 1H, pz-H3), (dd, 1H, pz-H5), (d, 1H, pz-H6), (*resid.* s, ph-H2/H6), (*resid.* s, ph-H3/H5), (s, 3H, methyl).

[$D_6$]-Htolpztr **12e**: Mass spectroscopy $HM^+$ ion at 244 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: 9.33 (*resid.* s, pz-H3), 8.77 (*resid.* s, pz-H5/H6), 7.34 (d, 2H, ph-H2/H6), 8.00 (dd, 2H, ph-H3/H5), 2.36 (*resid.* m, methyl). $^2D$ NMR in ([$H_6$]-DMSO) δ ppm; 9.34 (pz-D3), 8.74 (pz-D5/D6), 2.28 (Methyl-).

[$D_7$]-Htolpztr **12f**: Mass spectroscopy $HM^+$ ion at 245 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: 9.33 (d, 1H, pz-H3), 8.77 (m, 1H, pz-H5/H6), 7.34 (*resid.* s, ph-H2/H6), 8.00 (*resid.* s, ph-H3/H5) 2.36 (*resid.* m, methyl).

[$D_{10}$]-Htolpztr **12g**: Mass spectroscopy $HM^+$ ion at 248 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: 9.33 (*resid.* s, pz-H3), 8.77 (*resid.* s, pz-H5), (*resid.* s, pz-H6), 7.34 (*resid.* s, ph-H2/H6), 8.00 (*resid.* s, ph-H3/H5), 2.36 (*resid.* m, methyl)

*Pyridine-1,2,4-triazole based compounds*

[$D_5$]-Hpytr **13b**: Mass spectroscopy $HM^+$ ion at 151 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: 8.09 (*resid.* s, py-H3), 7.98 (*resid.* s, py-H4), 7.51 (*resid.* s, py-H5), 8.70 (*resid.*s, py-H6), 8.27 (*resid.* s, tr-H5). $^2D$ NMR in ([$H_6$]-DMSO) δ ppm; 7.99 (py-D3), 7.88 (py-D4), 7.51 (py-D5), 8.71 (D6), 8.12 (tr-D5)

[$D_7$]-Hmepytr **14b**: Mass spectroscopy $HM^+$ ion at 168 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: (*resid.* s, py-H3), (*resid.* s, py-H4), (*resid.* s, py-H5), (*resid.* s, py-H6), (*resid.* m, Methyl). $^2D$ NMR in ([$H_6$]-DMSO) δ ppm; 7.96 (py-D3), 7.84 (py-D4), 7.38 (py-D5), 8.58 (py-D6), 2.26 (Methyl)

[$D_1$]-Hphpytr **15b**: Mass spectroscopy $HM^+$ ion at 224 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: (d, 1H, py-H3), (dd, 1H, py-H4), (dd, 1H, py-H5), (*resid.* s, py-H6), (d, 2H, ph-H2/H6), 7.54 (dd, 2H, ph-H3/H5) 7.49 (t, 1H, ph-H4), $^2D$ NMR in ([$H_6$]-DMSO) δ ppm; 8.67 (py-D6)

[$D_4$]-Hphpytr **15c**: Mass spectroscopy $HM^+$ ion at 227 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: (*resid.* s, py-H3), (*resid.* s, pz-H4), (*resid.* s, py-H5), (*resid.* s, py-H6), (d, 2H, ph-H2/H6), 7.54 (dd, 2H, ph-H3/H5) 7.49 (t, 1H, ph-H4), $^2D$ NMR in ([$H_6$]-DMSO) δ ppm; 8.09 (py-H3/H4), 7.49 (py-H5), 8.70 (py-H6).

[$D_5$]-Hphpytr **15d**: Mass spectroscopy $HM^+$ ion at 228 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: (d, 1H, py-H3), (dd, 1H, py-H4), (dd, 1H, py-H5), (d, 1H, py-H6), (*resid.* s, ph-H2/H6), 7.54 (*resid.* s, ph-H3/H5) 7.49 (*resid.* s, ph-H4).

[$D_9$]-Hphpytr **15e**: Mass spectroscopy $HM^+$ ion at 232 m/z. $^1H$ NMR ([$D_6$]-DMSO) δ in ppm: (*resid.* s, py-H3), (*resid.* s, py-H4), (*resid.* s, py-H5), (*resid.* s, py-H6), (*resid.* s, ph-H2/H6), 7.54 (*resid.* s, ph-H3/H5) 7.49 (*resid.* s, ph-H4). $^2D$ NMR in ([$H_6$]-DMSO) δ ppm; 8.08 (py-H3/H4), 7.48 (py-H5, ph-H3/H5/H4), 8.70 (py-H6), 8.01 (ph-H2/H6).